

Chlorate Oxygen Generator (Oxygen Candle)
Review of the History of Candle Development
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I. INTRODUCTION

"At any time and without warning, a submarine may have to remain submerged for several days on account of the presence of the enemy, or rough weather, or serious accident to the machinery. Fortunately such occurrences are rare; but every commanding officer must be prepared to meet such an emergency that will afford his men the greatest possible chance of survival." Reference (1)

This quotation is taken from a review of submarine air purification technology published by the Bureau of Medicine and Surgery in 1919. At that time, the U.S. Navy had just begun to experiment with possible air purification devices and supplies of oxygen that might permit submarines to remain submerged longer than the untreated closed atmosphere would allow. Submariners were exposed to elevated levels of carbon dioxide and reduced levels of oxygen that would be considered completely unacceptable by current standards. It was a different world, but humans are still humans, and the requirements for safe and effective functioning in a self-contained environment are really unchanged. The maximum submergence time for submarines as published in that work was approximately 48 hours, reference (1)

In early submarines, the preferred supply of oxygen was 1800 psig compressed gas bled into the boat as needed, references (1,2). The need for added oxygen was occasionally "measured" by the physiological impact on the crew rather than a reliable instrument, reference (1). The design of submarine oxygen supply was limited to approximately 25 day submerged operation, reference (2). It was not until 1958 that U.S. submarines were able to carry out dives beyond that period and necessitated new sources of oxygen, reference (2). A curious second source of oxygen at the time was compressed air vessels that were bled into the boat while "vitiating" air (air with reduced oxygen and elevated carbon dioxide) from the opposite end of the boat was compressed into waiting empty vessels, reference (1). The periodic use of pressurized air to control oxygen caused swings in ambient pressure that was uncomfortable to the crew, reference (1). As early as 1919, liquid oxygen was a commercially available product and its use on submarines was contemplated, reference (1). It is interesting that even at this date, 1919, the danger of oils or greases when exposed to compressed or liquid oxygen was recognized:

"One precaution must be always taken. No oil or grease should be used in the gauge or fittings or a dangerous explosion may result." Reference (1)

II. SOLIDS AS A SOURCE OF OXYGEN

As submarines were required to accomplish longer and longer submerged periods of operation, the need to manage normal and emergency life support supplies became a priority. Sodium chlorate candles are a very efficient means of storing oxygen with a mass of oxygen per unit of volume greater than compressed oxygen (unless the pressure is above roughly 4,000 psig), reference (5). The volume efficiency of candles is almost equal to that of liquid oxygen without the dangers and equipment issues of cryogenic storage, references (3 and 8). These devices are known by several names: Oxygen Candles, Chlorate Candles, SCOG (either Solid Chemical Oxygen Generator or Self-Contained Oxygen Generator) and SFOG (pronounced "S-FOG," Solid Fuel Oxygen Generator).

The use of chlorates or perchlorates as sources of oxygen dates from at least 1930 when emergency oxygen supplies manufactured in Berlin for miners were described, references (4 and 5). During World War II, the Japanese introduced a chemical oxygen generator for aircraft pilot use. Both of those devices had serious shortcomings because they generated oxygen contaminated with excessive amounts of chlorine and carbon monoxide, references (4 and 5). The early Japanese candles actually used carbon as the sacrificial energy source leading to much higher amounts of carbon monoxide and dioxide being produced, reference (4). By 1945, sodium chlorate oxygen candles had been improved and had been tested aboard the USS Sailfish, reference (3). The candles were developed in part at the Naval Research Laboratory (NRL), reference (4) and the Oldbury Electro-Chemical Corporation, references (4 and 5) and were considered as a supplementary oxygen supply to the high-pressure oxygen banks, reference (3). Mine Safety Appliances Company worked on developing efficient manufacturing processes and development of a suitable burning apparatus and ignition method, reference (4). These "candles" were very much like those still in use today being a mixture of primarily sodium chlorate, iron powder, barium peroxide and glass fiber binder. The advent of the nuclear-powered submarine provided sufficient electrical power to make production of oxygen by water electrolysis the ideal source of oxygen, reference (3). Chlorate candles remained as an alternative or emergency source of breathing oxygen, reference (5).

The early potassium chlorate candles from Japan and Germany were deemed by the U.S. Navy as not suitable for military use because they generated oxygen contaminated with excessive amounts of chlorine and carbon monoxide, reference (4). The work by NRL and Oldbury Electro-Chemical identified barium peroxide as an effective chlorine scavenger. Approximately 4%wt barium peroxide was added to the candle mixture and greatly reduced the chlorine output, reference (4). Carbon monoxide is greatly reduced by careful use of purified carbon free iron as the fuel, reference (5). The U.S. Navy pursued the use of sodium chlorate in the place of potassium chlorate since it produces a higher yield (on mass basis) of oxygen and functions at lower temperatures.

III. CHEMICALS AND CHEMISTRY OF SOLID OXYGEN SOURCES

The most common commercial and military chemical oxygen generating candles are primarily composed of sodium chlorate, NaClO_3 . This material melts at approximately 248°C (478°F) and decomposes at 478°C (892°F), reference (8). Other chemicals occasionally used or mixed

together are sodium perchlorate (NaClO₄), potassium chlorate (KClO₃), potassium perchlorate (KClO₄), lithium chlorate (LiClO₃), and lithium perchlorate (LiClO₄), reference (8). Table 1 lists the most common materials that have been or could be used as a source of chemically generated oxygen along with their melting and decomposition temperatures.

The release of oxygen from either chlorates or perchlorates requires raising the material to substantial temperatures. The reactions are generally exothermic, but an additional energy source is generally required to form a sustained reaction. Increasing the reaction temperature increases the rate of oxygen production, reference (4).

Table 1. Basic Chemical Data for Most Common Sources of Chemical Oxygen

Name	Formula	Weight	% oxygen*	T melt**	T decomp**
Sodium chlorate	NaClO ₃	106.4	45%	248°C 261°C	478°C
Sodium perchlorate	NaClO ₄	122.4	52%	266°C 471°C	480°C 482°C
Potassium chlorate	KClO ₃	122.5	39%	368°C 357°C	400°C
Potassium perchlorate	KClO ₄	138.5	46%	525°C 588°C	400°C***
Lithium chlorate	LiClO ₃	90.4	53%	129°C	270°C
Lithium perchlorate	LiClO ₄	106.4	60%	236°C 247°C	430°C 410°C

* Percentage by mass based on a molecular weight calculation.

** From references 6, 7 and 8. Multiple values from different sources.

*** Decomposition occurs before solid melts.

Table 2. Standard Heat of Formation and Heat of Reaction for Oxygen Production

Name	Reaction (one mole reactant)	ΔH_f° (reactant)*	ΔH_f° (chloride)	ΔH_r° (kJ/mole)**
Sodium chlorate	$\text{NaClO}_3 \rightarrow \text{NaCl} + 3/2 \text{O}_2$	- 366*** [- 358]	- 411 [- 409]	- 45 [- 51]
Sodium perchlorate	$\text{NaClO}_4 \rightarrow \text{NaCl} + 2 \text{O}_2$	- 383 [- 384]	- 411 [- 409]	- 28 [- 25]
Potassium chlorate	$\text{KClO}_3 \rightarrow \text{KCl} + 3/2 \text{O}_2$	- 398	- 436 [- 435]	- 38 [- 37]
Potassium perchlorate	$\text{KClO}_4 \rightarrow \text{KCl} + 2 \text{O}_2$	- 433 [- 430]	- 436 [- 435]	- 3 [- 5]
Lithium chlorate	$\text{LiClO}_3 \rightarrow \text{LiCl} + 3/2 \text{O}_2$	- ****	- 409	- ****
Lithium perchlorate	$\text{LiClO}_4 \rightarrow \text{LiCl} + 2 \text{O}_2$	- 381 [- 380]	- 409	- 28 [- 29]

- * Standard Heats of Formation from reference (6) in units of Kilojoules per gram-mole, and compared favorably with values from reference (9) in brackets.
- ** Standard Heat of Reaction calculated based on balanced equation. (Standard Heat of Formation for O₂ in gaseous state is defined as 0.0.)
- *** Negative heat of reaction indicates an exothermic (heat given off) reaction.
- **** Heat of formation for lithium chlorate not found, heat of reaction not determined.

Table 3. Standard Heat of Formation and Heat of Reaction for Iron Reactions

Reaction (one mole reactant)	ΔH_f° (Iron oxide)*	ΔH_r° (per mole iron)	ΔH_r° (per gram iron)
$\text{Fe} + 1/2 \text{O}_2 \rightarrow \text{FeO}$	-272 **	-272 ***	-4.87
$\text{Fe} + 3/2 \text{O}_2 \rightarrow 1/2 \text{Fe}_2\text{O}_3$	-824	-412	-7.38
$\text{Fe} + 2/3 \text{O}_2 \rightarrow 1/3 \text{Fe}_3\text{O}_4$	-1118	-373	-6.68

- * Standard Heat of Formation from reference (6) in units of Kilojoules per gram-mole.
- ** Standard Heat of Reaction calculated based on balanced equation. (Standard Heat of Formation for O₂ in gaseous state is defined as 0.0.)
- *** Negative heat of reaction indicates an exothermic (heat given off) reaction.

Early studies measured the heat produced to be approximately 200 calories released per gram of candle mixture, references (4 and 8). Those tests were performed on small candle sample of similar composition to current candles. That value converts to approximately the 9,500 BTU per candle given in the Atmosphere Control Manual, reference (10). The second source of the 200 calorie value, reference (8), also stated that iron burning candles generate approximately 3.7×10^6 Joules/m³ of oxygen produced. That value converts to approximately 11,000 BTU for a 115 SCF oxygen candle. Based on the approximate value of the numbers, the values of 200 calories per gram of candle and 3.7×10^6 Joules/m³ of oxygen can be considered as in agreement.

The actual temperature of the reaction zone varies somewhat from reference to reference. Typical values given range from 538°C, reference (8), to 700°C -800 °C, reference (5) to 800°C - 900 °C, reference (11). The generally accepted value is approximately 500-600 °C. The higher values sometimes for higher percentages of iron in the ignition zone. A video provided by Molecular Products, reference (12) shows the ignition and burning of a small candle. The top zones of the candle with high iron content are clearly red hot, while the "normal" zone does not appear red indicating a lower temperature. The larger the diameter of a candle increases the internal temperatures due to lower heat transfer. The maximum temperature measured at the reacting front ranged from 740 °C for a 4.1 cm diameter one to 802 °C for an 11.1 cm candle, reference (4). Candle material transfers heat poorly. Un-insulated candles burned in open air produced a temperature of over 700°C at the burning front, but were below 100°C just 10 millimeters (0.4 inches) from the front, reference (4).

Measurement of actual oxygen production for a candle indicate that approximately 94% of the potential theoretical oxygen bound in the chlorate is released by the candle, reference (4). The

theoretical fraction of oxygen that should be removed by the oxidation of the 10% wt iron powder is 12%. This would leave 88% of the available oxygen for delivery. This discrepancy (94% measured versus 88% theoretical) implies that either the iron is converting to FeO rather than Fe₂O₃ or Fe₃O₄ or only part of the iron is reacting. Tests have shown that one third to one half of the available iron is not reacted as indicated by the residual being magnetic, reference (4). Additional iron beyond approximately 10% by weight does not further decrease the amount of oxygen released indicating that the additional iron is not reacting at all.

There is, however, a lower limit to the amount of iron needed to insure a continued candle burn. This amount is strongly dependant on the geometry of the candle and the resulting heat loss to the surroundings relative to heat generation rate, reference (4). For a candle of similar geometry to the current Navy candle, 2, reference (8) to 5% wt, reference (4) reduced iron powder is approximately the minimum that permits continued combustion.

IV. IMPURITIES IN OXYGEN PRODUCT

Because of the presence of some carbon in the iron (or steel fibers) both carbon dioxide and carbon monoxide are formed. The use of reduced iron powder as opposed to steel wool lowers the amount of both carbon gases. Early US furnaces were equipped with Hopcalite filters to convert the more hazardous carbon monoxide to carbon dioxide, reference (5). The current British SCOGs have an internal Hopcalite (Moleculite) filter, reference (12). Hopcalite acts as a catalyst for the carbon monoxide conversion and is not consumed in use.

Residual water, references (8, 13,14, and 15) from manufacturing can lead to formation of hypochlorous acid (HOCl), reference (11) or Cl₂ or ClO₂, reference (8). The use of asbestos as the binder generated higher levels of chlorine in the exhaust, references (5 and 14). The effect of the asbestos was attributed to "water of crystallization" in the asbestos, reference (5). Those chlorine producing side reactions become more serious as the reaction temperature increases, reference (8). The chlorine appears to be generated in the candle interior where the temperature is highest and gas species may be trapped briefly before escaping, reference (14). A small amount (3% wt -5% wt) of barium peroxide is added to the candle mixture as a scavenger for HOCl and free chlorine that appears to be generated by the formation of Na₂O in a minor side reaction, references (8 and 14). While performing this function, the barium peroxide releases additional oxygen, reference (4) and heat, reference (14). Internal candle temperature measurements have shown that the presence of barium peroxide increases the candle internal temperature and thereby increases the rate of oxygen production, reference (4). Early oxygen candles with approximately 5% barium peroxide from MSA produced an average of 5 ppm chlorine over their entire burn, reference (5). This value was derived by averaging gas detector tube readings taken periodically during the candle burn. The detector tubes were difficult to use since the indicator color tended to become bleached and difficult to interpret indicating the possible presence of chlorine-oxygen compounds, reference (5). The Hopcalite filter for carbon monoxide treatment also was found to remove chlorine, reference (5). Hopcalite irreversibly absorbs the chlorine and will become steadily less active toward both chlorine and carbon monoxide over time. Cobalt hydroxide (Co(OH)₂) has been tested and shown to be effective as a possible replacement for barium peroxide, reference (8).

For the application of the oxygen candle to the submarine where the oxygen is diluted throughout the vessel, the levels of carbon monoxide and chlorine (all species together) are not a hazard at the levels normally generated by candles, reference (11). The current specification for US Navy candles, reference (16), places a limit of 25 ppm carbon monoxide and 2.5 ppm chlorine (all species) averaged over the entire burn. A significant portion of both impurities are generated during the ignition phase or first 5 minutes, references (11 and 17). Typical peak levels of impurities seen during ignition are 150 (reference 17) - 250 (reference 11) ppm carbon monoxide and 20 (reference 11) - 30 (reference 17) ppm Cl_2 . The use of solid chemical oxygen generators that directly feed personnel (emergency oxygen supply in airplanes) must filter the oxygen since it is breathed directly by the user.

V. METAL OXIDES AS CATALYSTS.

It has been long known that the presence of various metal oxides function as catalysts for the decomposition reaction, reference (4). A catalyst would lower the reaction temperature for releasing oxygen and could lower the amount of iron fuel needed. Lower iron amounts would permit additional oxygen to be produced by the candle. A lower temperature candle would be inherently safer and most likely generate lower amounts of chlorine contaminant, reference (8). A goal has long been to develop a no-fuel candle that uses the small exothermic heat from the decomposition reaction and careful management of heat loss to eliminate the need for metal fuel. The metal compounds (oxides, sulfates, chlorides in various cases) identified include manganese, references (8, 11, 20, 24, 25, 26, and 27), copper, references (8, 11, 24, 25, 26 and 27), cobalt, references (8, 23, 24, 26, 27 and 28), nickel, references (8, 24, 25, 26, 27, 28), chromium, references (24 and 26) and tin, reference (28). Some of these metals (especially tin, nickel and cobalt can serve as a fuel (starting in the pure state) and catalyst removing the need for the iron. Iron itself is known to act as a catalyst decreasing the decomposition temperature compared with heated pure sodium chlorate.

The presence of these catalytic metal compounds caused the chlorate mixture to give off its oxygen at lowered temperatures. Generally, these experiments were performed by Thermogravimetric analysis in which the mass of a sample is continuously measured as the temperature is raised. The samples were mixtures of sodium chlorate (or other chlorate or perchlorate) and the metal compound (not the pure metal). The data showed the temperatures when the mass decreased due to oxygen production. Consistently, cobalt compounds produced the most significant decrease in temperature. As an example, 3.0% wt Co_3O_4 and sodium chlorate decomposed in the temperature range 240°C to 260°C , while a similar mixture with iron oxide decomposed in the range 300°C to 380°C and pure sodium chlorate 520°C to 580°C , reference (26). At least two patents have been issued for a cobalt catalyzed oxygen generator, references (22 and 23).

VI. MANUFACTURING PROCESSES

The candle manufacturing process involved thoroughly mixing the dry ingredients, moistening with 1.5% wt, reference (8) to 3% wt, reference (13) to 5% wt, reference (3) water and pressing with a high pressure ram. The higher the ram pressure the higher the final candle density. NRL performed tests from 5,000 to 24,000 psi. From 5,000 to 12,000 psig the density of the candle rose from 2.1 to 2.27 g/ml (an 8% increase). Increasing to 24,000 psig yielded a density of 2.4 g/ml (a further 6% increase), reference (13). The theoretical density of the sodium chlorate is approximately 2.7 g/ml. In order to remove water, the candles had to be heated throughout, without raising the exterior temperature too high. The original manufacturing process dried the molded candle 100°C, reference (4). The poor heat transfer within the candle led to long drying times of up to eight days, reference (14). Drying at 235°C also caused roughly 25% of the barium peroxide to give off oxygen. This is not thought to be a decomposition reaction, but a reaction between the barium peroxide and water forming barium hydroxide, reference (14). This small loss of oxygen is trivial compared with total candle capacity, and should also not inhibit the function of the barium in removing chlorine. A maximum oven temperature of 240°C is recommended, reference (14).

A second manufacturing process involving heating the initial mixture was proposed by Naval Research Laboratory (NRL), references (4, 5, 11, 13, 14, 15 and 21). The NRL process involved melting and casting or softening followed by pressing the semi-molten material into the final shape. The casting process yielded higher density material (23 lb for the cast candle versus 21.5 lb per pressed candle 6 inches diameter x 10 length) and reduced CO emission, reference (5). Softening at higher temperature allowed dense candle production at reduced pressures. At 225°C, a pressure of 10,000 psig was used, while at 240°C, only 5000 psig was needed, reference (14). Candles manufactured by either casting or hot pressing must be cooled slowly to avoid cracking of the finished product, references (11, 14). At 225 °C, candles nearly at the theoretical density could be formed, reference (13).

Heating the candle material proved time consuming due to poor heat transfer through the material and the necessity of using a low temperature heat source to avoid any decomposition. Naval Research Laboratory developed a process of heating a preformed candle by a radio-frequency coil mounted around a formed candle, references (11, 14 and 21). The radio energy coupled with the iron/steel fibers in the candle mixture. Iron powder did not absorb the radio energy efficiently, references (11, 14 and 21). Hot spots within the candle as it was being heated caused gas bubbles (probably oxygen) to form and be trapped leading to inconsistent oxygen generation when burning, reference (11).

Mine Safety Appliances Company found that the casting method was difficult to scale up to industrial quantities preferring to use the pressing method, references (5 and 13). One issue was that the metal powder or fibers clumped together in the melted material and also tended to sink through the material while being cast, reference (8). The clumping of the iron in molten chlorate could be addressed by adding small amounts of potassium chlorate, references (11 and 15). The high temperatures necessary for highest density product also lead to some decomposition of the material (bubbles forming). It was observed that a small addition (0.5% wt) of sodium perchlorate dramatically decreased the bubble formation, reference (14).

Currently, both manufacturers of Navy candles continue to use the wet high-pressure process.

VII. BINDER ADDITIVE

Since the chlorate material melts during the reaction, some inert material must be added to the candle to preserve its shape during use and as the clinker cools. Early candles used thermally stable asbestos fibers, reference (5). Due to concerns about the health effects in manufacturing and use, asbestos was replaced with steel wool or glass fibers. The presence of glass fibers helps the cooling clinker to maintain its shape and avoid cracking, reference (4). The older asbestos fibers, in addition to being a health and safety concern for all involves with candles, appears to increase the amount of chlorine generated, reference (8). Steel wool worked well, but contributed to the CO and CO₂ released since steels contain approximately 6% elemental carbon, reference (5). The current use of glass fibers provides the physical stability without increasing CO production.

VIII. IGNITION OF CANDLES, CURRENT PRACTICE

The ignition of the candles is aided by a high concentration of iron in an ignition section. The proportion of reduced iron in that zone is 20%wt, reference (4), to 30%wt, reference (8). Some candles also incorporate an elevated iron "booster" section at the top of the candle surrounding the ignition section with. This booster section serves to evenly ignite the cross section of the candle.

A. Red Phosphorous nail

Ignition by the red phosphorus tipped nail was employed as early as 1950, reference (4). The igniter "match" is a six inch long, nine gauge (approximately 5/32 inch diameter shaft) foundry nail. The head of such a nail is approximately 1/2 inch in diameter. The nail head is coated with red phosphorous by painting or dipping the head with phosphorus dissolved in a mixture of glue and acetone, reference (5).

The phosphorous igniter was found to be reliable at room temperature. For aircraft devices, the phosphorous proved to be inconsistent at low temperatures (-50°C), reference (4). A percussive igniter was developed for aircraft use that supplied approximately "800 calories of hot gas" to the candle igniter section, reference (4).

The prior version of the U.S. specification (drawing) for the chlorate candle specified that the igniter nail should have less than 0.1 grams of red phosphorous, reference (29). The potential for that statement to allow too little phosphorous to be applied was addressed in the current specification that gives a range of 0.04 to 0.1 grams of phosphorus, reference (16). The lower limit of 0.04 grams was computed on the basis of the heat of reaction of phosphorus forming P₂O₅ calculated to be -23.74 kilo-Joules/gram Phosphorus. The amount of heat needed was estimated as energy required to heat one cubic centimeter of candle mixture to the melting point, melting it and raising it to the decomposition temperature of pure sodium chlorate. The required

energy was estimated to be approximately 1000 joules leading to a requirement of 0.042 grams of red phosphorous.

B. Cartridge, Standard 0.410 Bore

The British (and Canadian) self-contained oxygen generator (SCOG) utilizes a bullet-less 0.410 bore cartridge and striker. The burning debris from the cartridge impacts the ignition end of the candle, or "brick," and begins the burn. NASA measured the production of some NO_x from this device, reference (30).

C. Thermite

NASA utilizes a similar self-contained oxygen generator, the Solid Fuel Oxygen Generator (SFOG), on International Space Station. Because of the NO_x emission measured with the cartridge igniter, they developed an igniter in the same cartridge that utilizes a mixture of aluminum and iron oxide powders. The cartridge primer, ignited by a physical strike, sets the exothermic reaction off. This type of igniter generated much lower amounts of NO_x, reference (30).

IX. BRIEF HISTORY OF PROBLEMS

A. Burn Rate Irregularities

Candles were reported to burn at uneven rates, occasionally tripling their generation rate. This behavior is attributed to incomplete mixing of the iron powder into the bulk chlorate, reference (9).

B. MIR fire

The Russian MIR space station carried a lithium perchlorate oxygen generator designated TGK. In 1997 one TGK unit failed having burned through the thin stainless steel wall. It is assumed that the stainless steel was actually burning in the high temperature oxygen stream. The fire continued for some 10-20 minutes until the generator was exhausted. NASA assisted the Russian Space Agency with the failure investigation.

The investigation concluded that the oxygen generator was probably contaminated during manufacture. The contaminant being either a hydrocarbon material or a fragment of the manufacturer's technician's chemical gloves reference (31). The fire of the stainless steel shell was due in part to its extreme thinness since thinner metals have been shown to be more flammable in elevated oxygen compatibility tests, reference (32).

C. ValuJet Flight 592

ValuJet Flight 592 crashed into the Florida Everglades in May, 1996. The cause of the crash and loss of all aboard was due to one or more expired airline oxygen generators accidentally activating

in the cargo hold of the plane. The oxygen generators were expired (but not expended) units from another aircraft carried as cargo. New generators are required to have safety caps that preclude accident ignition. Those caps are removed when they are installed in an aircraft and the caps apparently disposed of since they are not placed generators when they are removed. The crew removing these expired ones did not have extra caps available to place on them. Therefore the generators were without their normal backup safety to prevent accidental ignition. Once ignited, the heat released by the generators and the oxygen enriched atmosphere lead to a rapidly spreading and intensely hot fire. The fire spread to the passenger compartment and cockpit and apparently destroyed the flight control mechanisms. Many changes were recommended by the accident investigation board including smoke detectors and fire suppression systems in cargo spaces, design of special heat resistant packaging for oxygen generators and not permitting transport of oxygen generators aboard passenger aircraft, reference (33).

D. USS Seawolf

Seawolf (SSN 575) experienced two "explosive" candle furnace fires in 1985. The report stated:

"The fires occurred approximately 15 minutes after ignition. The start of the first fire was accompanied by an explosion internal to the furnace. Five explosions occurred during the second fire. Both fires generated intense heat and heavy smoke resulting in zero visibility in the space. The flames in the second fire shot out from the bottom of the furnace, deflected off the deck plates and reached the compartment overhead." Reference (33)

The crew reported:

"The interior and exterior of the candle shipping/storage cans were clean. The candles had no discoloration or other apparent abnormality. The furnaces were clean and free of external contamination, having been in use for two days prior to the fires. The furnaces were of standard construction with the exception of the chimneys [*referring to candle basket*] which were manufactured by Mare Island Naval Shipyard of 078 mild steel." Reference (34)

The experiments by the Naval Research Laboratory showed that only hydrocarbon contamination could have caused the fire and pressure buildup as described by the crew. Although the crew reported no contamination, it was concluded that hydrocarbon contamination must have occurred. The mild steel basket was consumed in the fires, and NRL duplicated that result with their contaminated candle tests, reference (35).

E. HMS Tireless

The British submarine HMS Tireless experienced an explosion of a SCOG (Self-Contained Oxygen Generator) in March 2007 that resulted in the deaths of two seamen. NASA White Sands Test Facility offered to provide their expertise to evaluate the details of the explosion and to investigate the possible causes. The conclusions to the investigation were that the internal chlorate "brick" had become contaminated with hydrocarbon material. In addition, the brick was

probably cracked possibly due to rough handling. Investigation by the Royal Navy team showed that a large number of SCOGs were contaminated on the outside by various oils. In addition, the seal of the SCOG has been shown to leak if handled roughly. The crew of the Tireless and other submarines had reported that other SCOGs had exhibited swelling when burned, holes burning through the stainless steel SCOG wall, rattling sound while burning, and sparks or flames coming from oxygen outlet while burning, reference (36). NASA was able to substantially replicate the SCOG explosion, reference (37).

F. HrMs Bruinvis

Dutch submarine HrMs Bruinvis had a candle furnace over-pressure event in May 2007. The lid of the furnace blew open approximately 30 minutes after ignition. The operator reported that five candles had just been burned. He noticed that the pressure gage indicated "2.5 bar." The gage is graduated in bars above atmospheric pressure. A bar is equal to 14.5 psig, so the reading of 2.5 bar is equivalent to 36.2 psig. The operator watched as the pressure fell to "1 bar" (14.5 psig) and then left the space. The lid of the Dutch furnace is sealed with an o-ring fitted flange clamped with four bolts (each tightened with a hand wheel). Two of the bolts were broken and two bent. The Molecular Products report issued by Mr. David Baines, reference (38), concluded that the salt coated filters caused sufficient backpressure to force the lid open. The Dutch furnace uses two filters similar to the U.S. design, but mounted outside the furnace and piped so that the salt collects on the inside. The filters on this furnace did show significant salt layers, reference (38).

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